

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

(19) JAPANESE PATENT OFFICE (JP)

(12) Publication of Unexamined Patent Application (A)

(11) Japanese Patent Application Disclosure Number: H 02-155225

(43) Disclosure Date: June 14, 1990

(51) Int. Cl. <sup>5</sup>	Identification Code	JPO File No.	
H 01 L 21/205		7739-5F	
31/04		7522-5F	H 01 L 31/04 Y

Request for Examination: Not requested      Number of Claims: 2      (5 pages total)

---

(54) Title of the Invention: Method for Forming Amorphous Semiconductor Thin Film

(21) Application Number: S 63-308909

(22) Filing Date: December 8, 1988

(72) Inventor: Yoshinori Ashida  
1541 Yabecho, Totsuka-ku, Yokohama-shi, Kanagawa-ken

(72) Inventor: Nobuhiro Fukuda  
2882 Iijimacho, Sakae-ku, Yokohama-shi, Kanagawa-ken

(72) Inventor: Kenji Miyachi  
2882 Iijimacho, Sakae-ku, Yokohama-shi, Kanagawa-ken

(71) Applicant: Mitsui Toatsu Chemicals Inc.  
3-2-5 Kasumigaseki, Chiyoda-ku, Tokyo

## Specification

### 1. Title of the Invention

Method for Forming Amorphous Semiconductor Thin Film

### 2. Scope of Claims

(1) A method for forming an amorphous semiconductor thin film, comprising: a film forming process whereby a semiconductor thin film is formed on a substrate by the thermal decomposition of silane compound represented by the general formula  $\text{Si}_n\text{H}_{2n+2}$  (where  $n$  represents a natural number), a plasma treatment process whereby said formed thin film is exposed to a plasma of reactive compound gas having non-depositing properties, and a process whereby these operations are performed repeatedly.

(2) A method according to Claim 1, wherein the thickness of the thin film formed by thermal decomposition of the silane compound in one repeated operation in the step whereby the processes of using film growth and plasma are repeated is 3 to 1000 Å.

### 3. Detailed Description of the Invention

(Technological Field)

The present invention relates to a technique for improving quality of amorphous thin films, and by extension, a technique for the improvement of quality in amorphous solar cells that are composed of such thin films.

(Background Art)

Amorphous solar cells have already the new lives as low-output energy sources for driving portable calculators and watches. Nevertheless, they have been insufficient in terms of performance and stability as energy sources having large output, and serious studies have been carried out inward to improve their performance.

Thus, the photovoltaic conversion efficiency of a solar cell is expressed as the product of the open terminal voltage, short-circuit current, and curve factor. As result of various studies, theoretically predicted values have been approached in solar cells using presently available amorphous semiconductor thin films with respect to short-circuit current and curve factor. In order to improve the reliability of the solar cell, in recent years a pin type amorphous solar cell has been proposed in which a p-layer is provided on the light incident side, and in addition, a tandem-structure solar cell has been studied as a high-field type solar cell. Nevertheless, in present amorphous solar cells, as described above, there is a limit to any marked improvement of performance including reliability from the present standards, and substantial improvement of characteristics of the amorphous semiconductor thin film itself are necessary.

The present inventors, as a result of various studies and research, found that the characteristics of the

amorphous semiconductor films used in photoactive layers greatly restrict their reliability and conversion efficiency, and in particular, that the bonded hydrogen atoms contained in the semiconductor thin film determine the optical characteristics of semiconductor, and as a result the sunlight spectrum cannot be used efficiently, and that hydrogen atoms contribute to light instability whereby the solar cell performance produced by the irradiation of light is impaired. For this reason, reduction of the bonded hydrogen amount in the amorphous film in regular film forming methods (plasma CVD methods, optical CVD methods, thermal CVD methods, sputtering film formation methods, etc.) has been attempted, but it has been found that, rather than improving characteristics, by reducing the amount of bonded hydrogen, the number of defects in the film is increased, resulting in impaired film characteristics. In order to solve these problems, the present inventors based on further intensive studies achieved the present invention.

#### (Basic Concepts of the Invention)

Since bonded hydrogen plays an important role in compensating for defects, by increasing the substrate temperature during film formation, defects are actually induced due to thermal dissociation. The present inventors' basic concept is lies in the point that, film formation is performed under conditions where hydrogen is not bonded in the film, and subsequently bonding of hydrogen is performed in order to compensate for defects. As a result, as explained below in detail, with an extremely low amount of bonded hydrogen, it is possible to obtain an amorphous semiconductor thin film having few defects and good optical reliability.

#### (Disclosure of the Invention)

Specifically, the present invention is a method for forming an amorphous semiconductor thin film, comprising: a film forming process whereby a semiconductor thin film is formed on a substrate by the thermal decomposition of silane compound represented by the general formula  $\text{Si}_n\text{H}_{2n+2}$  (where  $n$  represents a natural number), a plasma treatment process whereby said formed thin film is exposed to a plasma of reactive compound gas having non-depositing properties, and a process whereby these operations performed repeatedly.

The present invention is explained below in further detail.

In the present invention, the silane compounds used as the source gas for forming the semiconductor thin film are represented by the general formula  $\text{Si}_n\text{H}_{2n+2}$  (where  $n$  represents a natural number), and include monosilane, disilane, trisilane, tetrasilane, and the like. In terms of handling, monosilane, disilane, and trisilane are especially preferable.

Moreover, as the source gas, the aforesaid silane compound may be diluted by the introduction of a carrier gas such as hydrogen, fluorine, chlorine, or other reactive gas, or helium, argon, neon, or other inert gas. The additive ratio for dilution, as represented by the ratio of silane compound to additive gas, is in a range of 0.1 to 100% (volumetric ratio), and at least 1% should be used from the standpoint of film formation rate.

In the present invention, first, a semiconductor thin film is formed by the thermal decomposition of such

source gas. The specific conditions for thermal decomposition referred to here are discussed below, and there are no special restrictions with respect to the equipment used, such as a hot well, cold well type, or other device type. One example of a specific device used for implementing the present invention is shown in Figure 1. Further, the gas flow amount is normally in a range of approximately 1 to 200 sccm, and the reaction pressure range is approximately 15 mtorr to 760 torr, but is not limited thereto, and the flow amount and pressure may be selected freely in another range in accordance with the film formation rate. Needless to say, these conditions are not limiting conditions with respect to implementation of the present invention. The substrate temperature for thermal decomposition is in a range of 300 to 700°C, and a range of 400 to 600°C is especially desirable from the aspect of film formation time, taking into consideration the heat resistance of the substrate and film formation rate.

In the present invention, the thickness of the amorphous semiconductor thin film formed in one thermal decomposition [cycle] is 3 to 1000 Å.

In the present invention, a plasma treatment process, in which the thin film formed by the aforesaid film forming process is exposed to plasma of reactive compound gas having non-depositing properties, is continuously performed.

This plasma treatment process by reactive compound gas is a process whereby a non-depositing reactive gas that is different from the silane compound previously used is introduced into the reactor containing the substrate on which an amorphous semiconductor thin film has already been deposited to a specified thickness, a plasma of the reactive gas is generated on the substrate, and the surface of the thin film formed on the substrate is treated by this plasma. The term “non-depositing reactive gas” as used here refers to a gas compound containing hydrogen atoms or fluorine atoms, among which commonly used examples include hydrogen gas, hydrogen fluoride gas, fluorine gas, nitrogen trifluoride, carbon tetrafluoride, and the like. Mixtures of these gases may also be used. The flow amount of this non-depositing reactive gas is approximately 5 to 500 sccm. The pressure during this treatment process should be within a range at which plasma is generated, i.e., 20 mtorr to 760 torr. Generally, since a 13.56 MHz high frequency discharge or direct current discharge is used, for convenience a range of 50 mtorr to 5 torr is desirable and practical. The substrate temperature during plasma treatment should be the same or lower than the substrate temperature during film formation, ranging from room temperature to about 700°C. Increasing the temperature differential with the substrate temperature when forming the amorphous semiconductor thin film by thermal decomposition is not desirable from practical aspects, and 200 to 600°C is desirable.

Although there is of course no essential restriction to the overall thickness of the amorphous semiconductor thin film formed by the method of the present invention, when the characteristics of the amorphous semiconductor thin film formed are examined, or the film is used in practical application, a

specified thickness of approximately 2000 Å to 3 μm is desirable. Further, the time of 1 cycle of plasma treatment is approximately 1 second to 2 hours. A specified film thickness is obtained by repeating the thermal decomposition film deposition process and non-depositing gas plasma treatment process described above, and for this purpose the number of repetitions depends on the desired film thickness. Accordingly, in the evaluation of the characteristics of the thin film obtained, generally a film thickness of least 2000 Å is desirable, so the number of repetitions should be at least 2. Although there is no special restriction has to the maximum number of repetitions, it should be no more than 1000, preferably any more than 200.

After formation of the amorphous thin film by thermal decomposition, the time interval until plasma treatment by non-depositing gas (the deposition-treatment interval) varies according to such factors as the equipment form and dimensions and the vacuum exhaust system, normally is from 2 to 600 seconds, and preferably 2 to 180 seconds. Furthermore, in order to realize the effects of the present invention more effectively, an interval of 2 to 30 seconds is desirable. On the other hand, the time until the amorphous thin film is formed by thermal decomposition after plasma treatment should be from 1 to 120 seconds, preferably 1 to 30 seconds.

There are no special restrictions with regard to the substrate used in the present invention, so long as heat resistance is taken into account. A glass substrate material such as conventionally used blue plate glass, borosilicate glass, or quartz glass may be used as a light-transmissive substrate, but in addition metals or metals formed on the aforesaid glass may be used as substrate materials. Further, in order to form amorphous solar cells containing the amorphous semiconductor thin films of the present invention as constituent layers, it is possible to use a substrate on which a transparent electrode is formed on a glass substrate or a metal substrate as a solar cell substrate, and metal oxides such as tin oxide, indium oxide, and zinc oxide as well as transparent metals and the like may be used as transparent electrodes.

Next, the present invention is explained in greater detail through working examples.

#### (Working Example 1)

Example of a specific device used to implement the present invention is shown in Figure 1. This device is a substrate temperature control and device having high-temperature response which uses a cold image oven using an infrared lamp 2 as a heater for heating the substrate 10. The film deposition chamber 1 was made of quartz, the substrate 10 was placed in its center, and plasma-generating electrodes 4, 4' were arranged in a ring configuration in positions surrounding the substrate. The power source for generating plasma used a 13.56 MHz high frequency power source. In the film deposition process, the substrate was mounted on a susceptor 9, which held the substrate, and moved and set in the quartz chamber. After evacuation to a high degree of vacuum, the carrier gas was introduced, the substrate was heated, and at a substrate temperature of 450°C and a reaction pressure of 1.0 torr, the carrier gas (here argon) was switched, 10 sccm disilane was introduced as

the source gas, and a 100 Å amorphous thin film was formed. Next, the temperature was raised to 300°C, hydrogen gas was introduced at 100 sccm for cooling, the pressure was set at 0.2 torr, plasma was generated by applying high-frequency power of 50 W, and plasma treatment was performed on the surface of the amorphous thin film for 30 seconds. Next, the substrate temperature was raised again to 450°C while the argon carrier gas was introduced, and amorphous thin film was deposited under the same conditions as before in the same thickness, and then plasma treatment was performed using the previously described non-depositing gas. This process was repeated 40 times, and a thin film having the specified thickness of 4000 Å was obtained. The substrates used here were a quartz glass substrate and single-crystal silicon substrate. The amorphous thin film obtained was removed from the thin film deposition device and metallic electrodes were formed. The quartz substrate was used for evaluation of optical characteristics and electrical characteristics of the amorphous thin film, and the single-crystal silicon substrate was used in measurement of the infrared spectrum.

As the film characteristics obtained by this method, the conductance (light conductance) under irradiation by simulated sunlight (AM-1.5) at 100 mW/cm<sup>2</sup> was  $2 \times 10^{-4}$  S/cm, the dark conductance was  $1 \times 10^{-11}$  S/cm, the optical band gap was 1.70 eV, the activation energy was 0.89 eV, and the bonded hydrogen amount was 5 at%.

In addition, the reliability of the amorphous semiconductor thin film obtained by the present invention was measured. As the method of measurement, continuous irradiation of simulated sunlight (AM-1.5) at 100 mW/cm<sup>2</sup> was performed for 20 hours, and reliability was based on changes in the light conductance. Using the light conductance after 20 hours in relation to the initial light conductance as the deterioration ratio, this amorphous semiconductor thin film had a value of 5%.

#### (Comparative Example 1)

In Working Example 1, an amorphous thin film only was formed by thermal decomposition to a specified thickness of 4000 Å, without performing hydrogen gas plasma treatment after the formation of the amorphous thin film by thermal decomposition. The characteristics of the thin film obtained by this method were light conductance  $6 \times 10^{-4}$  S/cm, dark conductance  $2 \times 10^{-10}$  S/cm, and bonded hydrogen amount 18 at%. These film characteristics are considerably lower than the film characteristics indicated for Working Example 1. Furthermore, as a result of measurement of reliability, the deterioration ratio was 40%, much lower than that in the working example.

#### (Effects of the Invention)

As is clear from the working example and comparative example, the amorphous semiconductor thin film produced using the present invention has excellent photovoltaic characteristics, and greatly improved stability with respect to light irradiation, which has been a substantial problem in the past. Specifically, in comparison with amorphous semiconductor thin films formed by conventional techniques, a thin film having extremely

high reliability is obtained, confirming the effectiveness of the film forming technique for amorphous semiconductor thin films according to the present invention. Specifically, by using the amorphous semiconductor thin film forming technique of the present invention, at a practical level, significant contributions are made to the improvement of the photovoltaic conversion efficiency of amorphous solar cells. Thus, the present invention contributes a technique which makes possible high conversion efficiency required in solar power cells, and must be considered an extremely useful invention to the energy industry.

#### 4. Brief Explanation of the Drawings

Figure 1 is a drawing which explains an example of an amorphous semiconductor thin film forming apparatus used to implement the present invention.

In the figure, 1... quartz chamber, 2... infrared lamp oven, 3... high-frequency power source, 4, 4'... high frequency electrodes, 5... voltage control valve, 6... turbo molecular pump, 7... oil rotary pump, 8... gas flow meter, 9... substrate susceptor, 10... substrate.



Figure 1